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Non-stoichiometry and defect structures in rapidly solidified MgO–Al₂O₃–ZrO₂ ternary eutectics

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Abstract

Rapid solidification of the two MgO–Al₂O₃–ZrO₂ ternary eutectics was accomplished by inductive heating followed by quenching with a twin roller device. The as-quenched materials exhibited diverse compositional and structural phase assemblages. A metastable binary eutectic between a spinel and zirconia phase was found in the Al₂O₃-rich eutectic composition and had the same composition of the Al₂O₃-rich ternary eutectic. Heat treatment of the samples yielded nucleation of γ -Al₂O₃ and then tetragonal zirconia (t-ZrO₂) at high temperatures as magnesium and oxygen ions diffused from the zirconia phase to the spinel phase. For the as-quenched MgO-rich eutectic, a spinel with nearly the stoichiometric composition formed with cubic-ZrO₂ and MgO. Close to the maximum amount of MgO was dissolved in the spinel and zirconia phases. Heat treatment resulted in diffusion of magnesium and oxygen ions out of the ZrO₂ phase and promoted the formation of tetragonal and monoclinic ZrO₂. © 1997 Elsevier Science S.A.

Keywords: Defect structures; MgO–Al₂O₃–ZrO₂; Rapid solidification

1. Introduction

Magnesium aluminate spinel (MgAl₂O₄) has been the subject of numerous scientific analyses due to the unusually wide range of stoichiometries it can possess over a wide temperature range. With a melting point of 2105°C, spinel is also an excellent refractory ceramic but, unfortunately, has poor thermal shock characteristics. It has potential use as an RF heating window in fusion reactors as well as for special case shapes in the steel industry due to its excellent permanent liner change and permanent volume change. Fabrication of a composite of spinel with zirconia (ZrO₂) could produce a ZrO₂-toughened, high-strength structural ceramic. The most well-known example of a ZrO₂ composite is ZrO₂-toughened Al₂O₃, a structural ceramic in which the toughening is provided by ZrO₂ present in the tetragonal form (t-ZrO₂), normally stable at temperatures greater than about 1170°C [1–3]. Re-

tention of this high-temperature polymorph at room temperature can be accomplished by several techniques, such as sol-gel processing and other chemical synthesis methods [4,5]. Rapid solidification (RS) is another technique in which ZrO₂ can be quenched directly into the t-ZrO₂ polymorph, resulting in a fine-grained microstructure. Rapid solidification of Al₂O₃–ZrO₂ binary systems has been well characterized [6–8] and the materials are used industrially as abrasives [9]. More significantly, it recently has been shown that a fine-grain size, dense, high-strength, high-toughness Al₂O₃–ZrO₂ composite can be fabricated from RS precursor powders [10].

Fig. 1 shows the ternary Al₂O₃–MgO–ZrO₂ phase diagram determined experimentally by Biereznoi and Kordyuk [11]. Two ternary eutectics and one binary pseudo-eutectic (along the ZrO₂–MgAl₂O₄ join) were identified, as shown on the diagram. Table 1 lists the compositions of the two ternary eutectics. One composition will be identified as Al₂O₃-rich (42.1 mol% Al₂O₃) and one will be identified as MgO-rich (42.1 mol% MgO). These two eutectics fall into compatibility trian-

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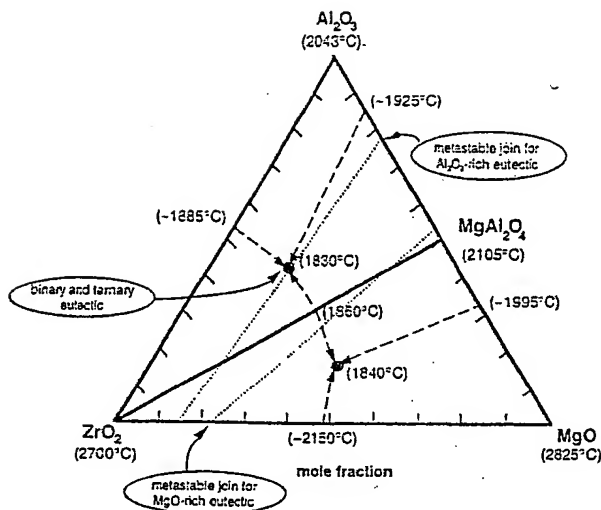


Fig. 1. The ternary Al_2O_3 - MgO - ZrO_2 phase diagram [11].

gles which both have MgAl_2O_4 and ZrO_2 as end members. Fig. 2(a) and (b) shows the binary phase diagrams for ZrO_2 - MgO [12] and MgO - Al_2O_3 [13], respectively. The ZrO_2 - MgO phase diagram shows that the ZrO_2 cubic phase field (c- ZrO_2) extends up to approximately 21 mol% MgO at $T \sim 2100^\circ\text{C}$. There is some confusion regarding the MgO - Al_2O_3 phase diagram in the Al_2O_3 -rich portion. Some experimental work reports a eutectic between spinel and Al_2O_3 [14-17] while thermodynamic modeling identifies a peritectic [13]. The thermodynamic modeling of the MgO - Al_2O_3 phase diagram shows surprisingly good agreement between experiment and theory across the whole compositional field and the phase diagram is considered to be the most reliable. The spinel phase, MgAl_2O_4 , displays a high degree of non-stoichiometry at $T \sim 2270^\circ\text{C}$ and can exist from 13.4 to 61.6 mol% MgO .

In this study, an extension of RS of the Al_2O_3 - ZrO_2 system was directed to the ternary eutectics in the Al_2O_3 - MgO - ZrO_2 system. Although quite a lot of research has been done on solid-state reactions in the binary systems (Al_2O_3 - ZrO_2 , ZrO_2 - MgO , MgO - Al_2O_3), the ternary system has not been widely studied. A wide range of non-stoichiometric spinels has been found in rapid solidification of MgO - Al_2O_3 compositions [18] and significant variations in MgO content can

be found in MgO -stabilized ZrO_2 . No work has been done on RS in the MgO - ZrO_2 system or in the Al_2O_3 - MgO - ZrO_2 system. It was the goal of this study to rapidly solidify the ternary eutectic compositions and study the as-quenched phases and the phase development during annealing.

2. Experimental techniques

Technical grade commercial powders of α - Al_2O_3 , monoclinic ZrO_2 (m- ZrO_2) and MgO were mixed according to the two eutectic compositions shown in Table 1 and then pressed to form rods of about 6 cm length and 1 cm in diameter. The rods were heated to 1200°C for 2 h to produce a more structurally robust body. The rods were then suspended in a 5-cm diameter graphite susceptor above a twin roller solidification device and were inductively heated by an RF generator. Liquid droplets formed on the end of the rod and were allowed to drop between the rollers rotating with surface speeds of about 1.6 m s^{-1} . This apparatus is ideally suited to RS experiments on eutectic compositions: details of the experimental apparatus are reported elsewhere [19]. The quenched materials were in the shape of thin foils ranging from 50 to 1000 μm in thickness and from 0.25 to 2 cm in length, depending on the processing and roller conditions. The solidified foil thicknesses were measured with a micrometer to $\pm 0.5 \mu\text{m}$. X-ray diffraction (XRD) was performed on powders obtained from crushing the 500- μm -thick solidification product. For annealing experiments, the as-quenched 500- μm -thick foils were heat treated for 1 h at temperatures between 800 and 1600°C and then crushed for XRD measurements.

3. Experimental results and discussion

3.1. As-quenched materials

Fig. 3 shows the XRD pattern from the as-solidified Al_2O_3 -rich eutectic. As shown, the peaks corresponding to the spinel phase and c- ZrO_2 do not match with the JCPDS standards due to the high concentration of MgO in ZrO_2 and low concentration in the spinel

Table 1
Compositions and melting temperatures of the two Al_2O_3 - MgO - ZrO_2 ternary eutectics [11]

	Compositions					Melting temperature (°C)	
	Al ₂ O ₃		MgO		ZrO ₂		
	mol%	wt. %	mol%	wt. %	mol%		wt. %
Al ₂ O ₃ -rich	42.1	43	17.4	7	40.5	50	1830
MgO-rich	16.6	20	42.1	20	41.3	60	1840

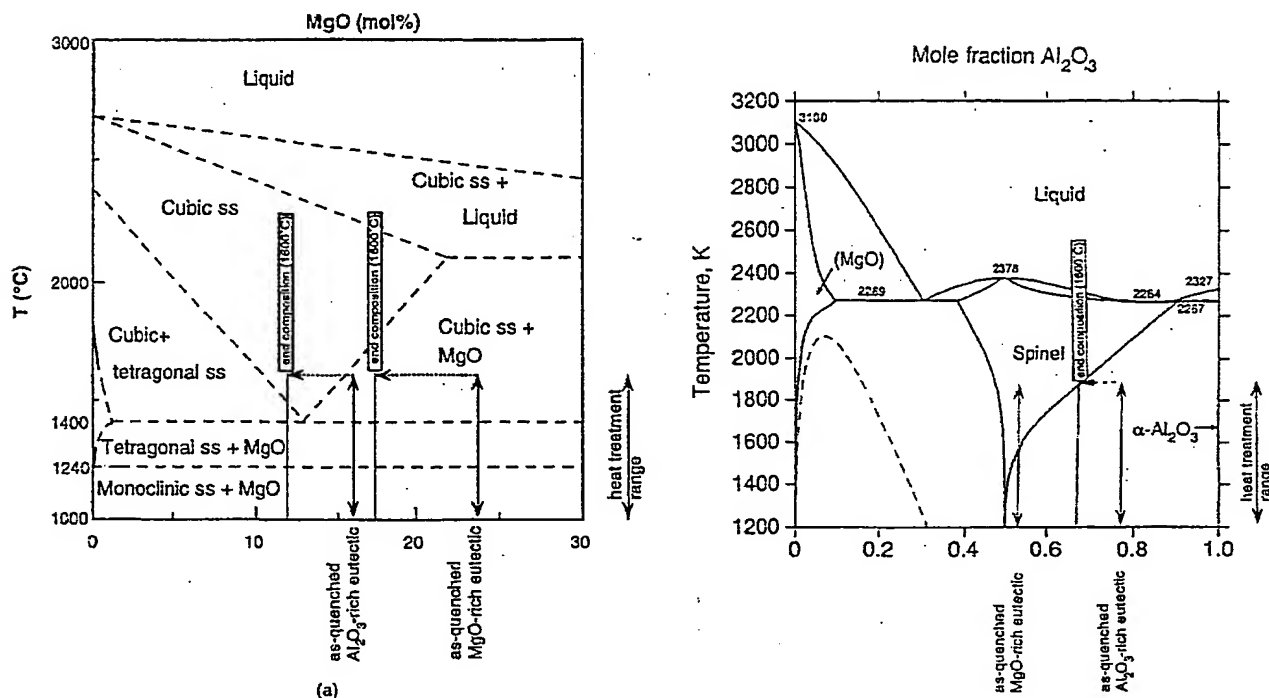


Fig. 2. Binary phase diagrams for (a) ZrO_2 - MgO [12] and (b) Al_2O_3 - MgO [13].

phase. The values of x in $\text{Mg}_x\text{Al}_{2(1-x)}\text{O}_{3-2x}$ ($0 \leq x \leq 0.5$, $x = C_{\text{MgO}}$ in spinel) and y in $\text{Mg}_y\text{Zr}_{1-y}\text{O}_{2-y}$ ($0.1 \leq y \leq 0.25$, $y = C_{\text{MgO}}$ in ZrO_2) phases were determined by the lattice parameters calculated from the XRD data. For non-stoichiometric spinels, the composition is often written as $\text{MgO} \cdot n \text{Al}_2\text{O}_3$. In the present case, $x = 1/(n+1)$, which is the mole fraction of MgO in the spinel. The lattice parameters calculated from the four most intense diffraction lines for both the spinel and c-ZrO_2 phases were averaged. Spinel and c-ZrO_2 are cubic and the relationship between d -spacings and the lattice parameter (a) is $d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}$.

For c-ZrO_2 , the Aleksandrov et al. [20] equation was used:

$$a_z = \frac{4}{\sqrt{3}} \left[R_{\text{Zr}} + R_{\text{O}} + \frac{\sum_k (P_k M_k \Delta R_k)}{1 + \sum_k M_k (P_k - 1)} \right] \quad (1)$$

where a_z = c-ZrO_2 lattice parameter, R_{Zr} , R_{O} , R_k are the ionic radii of zirconium, oxygen and the k -th stabilizing element, P_k is the number of ions of each stabilizing element in the oxide molecule, M_k is the mole fraction of the stabilizing element and ΔR_k is the difference between ionic radii of zirconium and the stabilizing element. According to Eq. (1), as the amount of stabilizing element is increased, the lattice parameter of ZrO_2 decreases due to the substitution of smaller ions on the Zr^{4+} sites. It is assumed that a negligible amount of Al_2O_3 is dissolved in ZrO_2 . Although it has been observed that in sol-gel-derived materials up to 40 mol% Al_2O_3 can be dissolved in ZrO_2 [21], this has not been observed in RS-derived materials [6-8]. The

radius of Mg^{2+} in the ZrO_2 lattice was calculated to be 0.0648 nm by using the lattice parameters tabulated for MgO -stabilized c-ZrO_2 from other data [22]. Substituting into Eq. (1) using $P_k = 1$, $r_{\text{Zr}} = 0.0824$ nm and $r_{\text{O}} = 0.1400$ nm, the lattice parameter (a_z) as a function of mole fraction of MgO (y) is:

$$a_z \text{ (nm)} = 0.5136 - 0.0407y \quad (2)$$

Chiang and Kingery [23] have determined the lattice parameter (a_s) of magnesium aluminate spinel ($\text{Mg}_x\text{Al}_{2(1-x)}\text{O}_{3-2x}$) as a function of MgO mole fraction, x :

$$a_s \text{ (nm)} = 0.7848 + 0.0470x \quad (3)$$

for MgO fractions from 0.20 to 0.50. The decrease of the spinel lattice parameter with increasing Al_2O_3 content is due to the creation of vacancies on the cation sublattice and to the substitution of the smaller Al^{3+} for the larger Mg^{2+} . In Ref. [23], it is possible that there was a depletion of magnesium in the samples, which would shift what was considered the stoichiometric spinel lattice parameter to a higher value, but da_s/dx should remain the same. In fact, the slope found in this experiment is identical to the one found by Sarjeant and Roy [18] for splat-quenched compositions of magnesium aluminate spinels.

Table 2 lists the XRD results for the as-quenched materials. For the Al_2O_3 -rich eutectic, under equilibrium conditions the phase assemblage should be $\text{Al}_2\text{O}_3 + \text{MgAl}_2\text{O}_4 + \text{ZrO}_2$. However, in the RS, materials nucleation of the Al_2O_3 primary phase was sup-

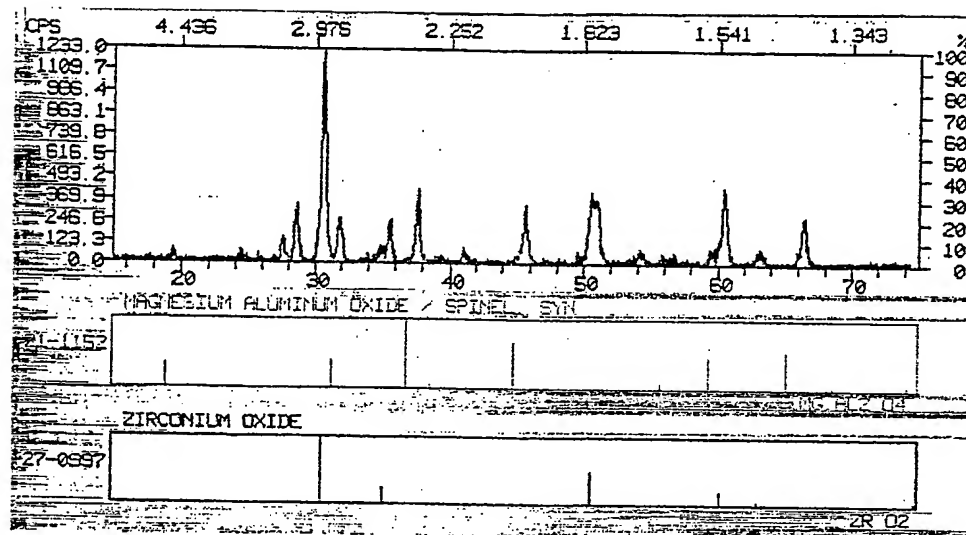


Fig. 3. X-ray diffraction pattern of the as-quenched Al_2O_3 -rich eutectic composition in comparison with the JCPDS standards for MgAl_2O_4 and c-ZrO_2 .

pressed and an Al_2O_3 -rich spinel ($x = 0.221$) and monoclinic (m) + c-ZrO_2 ($y = 0.155$) were found. The absence of one primary phase in the Al_2O_3 -rich system indicates that surface energy constraints limit the nucleation of that phase to decrease the total interphase boundary energy. It is not surprising that $\alpha\text{-Al}_2\text{O}_3$ formation is suppressed due to the lattice mismatch with the two other cubic phases. Fig. 4 shows a transmission electron micrograph (TEM) micrograph of the as-quenched Al_2O_3 -rich composition. The characteristic lamellar structure of a solidified eutectic is seen. There are only two phases observed; the light phase is the Al_2O_3 -rich spinel and the dark phase is ZrO_2 .

The presence of $m\text{-ZrO}_2$ ($\sim 10\%$) in the Al_2O_3 -rich composition can be explained by MgO vaporization from the surface of the liquid, and not from incomplete melting. If MgO vaporization occurred with simultaneous partial nucleation of unstabilized c-ZrO_2 (the high-temperature polymorph) on the surface of the droplet during melting, $m\text{-ZrO}_2$ would form after cooling to ambient temperature (see Fig. 2(a)). It has been shown in other works that substantial evaporation of MgO from ZrO_2 occurs at elevated temperatures [24,25] and is what likely occurred in the present case.

Table 2

Summary of the X-ray diffraction results on the as-quenched crystalline materials produced by twin rolling

Composition (mol%)	Phases present (mol% MgO)
42.1 Al_2O_3 -17.4 MgO -40.5 ZrO_2 (Al_2O_3 -rich)	Spinel (22.1), $m + c\text{-ZrO}_2$ (15.5)
16.6 Al_2O_3 -42.1 MgO -41.3 ZrO_2 (MgO -rich)	Spinel (46.2), $c\text{-ZrO}_2$ (22.2), MgO

For the MgO -rich composition under equilibrium conditions, the phase assemblage should yield $\text{MgO} + \text{MgAl}_2\text{O}_4 + \text{ZrO}_2$. In the RS material, a slightly Al_2O_3 -rich spinel phase ($x = 0.462$), MgO and c-ZrO_2 ($y = 0.222$) were found. Because of the high MgO content in the starting composition, $m\text{-ZrO}_2$ was not found, strengthening the argument that some MgO vaporization occurred during the melting and solidification experiment and the presence of $m\text{-ZrO}_2$ is not a by-product of partial melting.

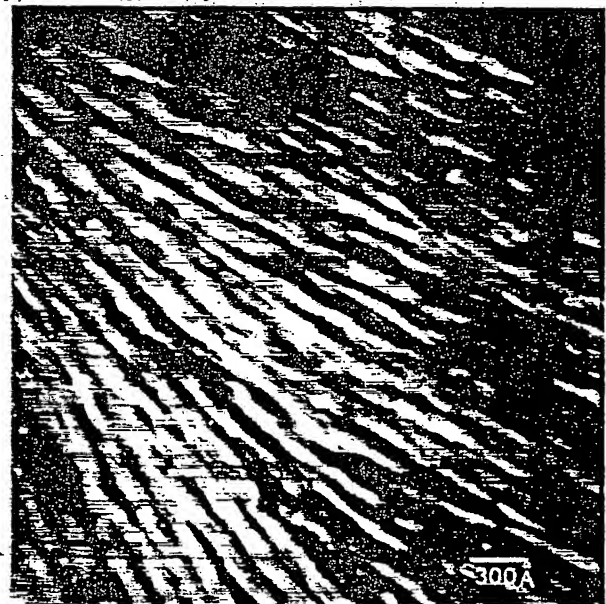


Fig. 4. TEM micrograph of the as-quenched Al_2O_3 -rich eutectic. The light phase is the MgO -depleted spinel and the dark phase is c-ZrO_2 .

Table 3

Molar phase contents of the rapidly solidified (RS) compositions compared with the equilibrium (Ξ) mixtures (determined from the phase diagram given in Fig. 1)

	Spinel (mol%)		ZrO ₂ (mol%)		Al ₂ O ₃ (mol%)		MgO (mol%)	
	Ξ	RS	Ξ	RS	Ξ	RS	Ξ	RS
Al ₂ O ₃ -rich	21.1	53.2	49.0	46.8	29.9	0	—	—
MgO-rich	19.9	30.8	49.5	53.1	—	—	30.6	16.1

Fig. 1 shows the compatibility relationships for the as-quenched phases. For the Al₂O₃-rich composition, the two end phases (Al₂O₃-rich spinel and c-ZrO₂) are connected by a metastable join containing a binary eutectic which has the same composition as the ternary eutectic. For the MgO-rich composition, the metastable compatibility triangle houses the ternary eutectic. The MgO-rich eutectic phase assemblage has a smaller fraction of the pure MgO phase with the balance incorporated into the c-ZrO₂ phase. It is interesting to note that even an excess of MgO does not promote the formation of a stoichiometric or an MgO-rich spinel. Table 3 lists the molar percentages of each phase in the RS material and are compared with what would be obtained under equilibrium conditions. For the Al₂O₃-rich composition, a higher fraction of spinel is found because all of the Al₂O₃ is dissolved in it: there is no pure Al₂O₃ phase. For the MgO-rich composition, a higher fraction of spinel and c-ZrO₂ is found due to the high concentration of MgO in each phase. The amount of the MgO phase is decreased from 30.6 mol% (under equilibrium conditions) to 16.1 mol% for the RS material.

It appears that significant supersaturation of MgO in ZrO₂ cannot occur through rapid solidification in these compositions. As seen in the binary phase diagram (Fig. 2(a)), c-ZrO₂ coexists with MgO in a compositional range of at least 12 mol% MgO at $T \geq 1400^\circ\text{C}$. During RS, it could be possible to suppress the nucleation of the MgO phase and thereby enrich the spinel and c-ZrO₂ with MgO. Assuming that even in the unlikely case that $x = 0.6$ (the maximum MgO content in spinel according to the equilibrium phase diagram), to maintain a mass balance this would require that $y = 0.30$, which roughly corresponds to the compound Mg₂Zr₅O₁₂. There was no experimental evidence found for this phase and, because of the presence of the MgO phase, indicates that supersaturation of MgO in ZrO₂ does not occur under RS conditions.

The spinel and c-ZrO₂ phases in both eutectics compete for MgO during the solidification process. In the Al₂O₃-rich eutectic, close to the minimum amount of MgO is dissolved in the spinel and ZrO₂ phases to maintain a spinel and c-ZrO₂ structure. The presence of ZrO₂ has been found to lead to an increase in solubility

of MgO in Al₂O₃ and that MgO preferentially dissolves in Al₂O₃ over that of ZrO₂ [26]. In the MgO-rich composition, close to the maximum amount of MgO is dissolved in the ZrO₂ and spinel phases, with the balance present as pure MgO.

3.2. Annealing experiments

Table 4 lists the phase development of the two ternary eutectics as a function of annealing temperature for 1-h anneals. For the Al₂O₃-rich composition, the Al₂O₃-rich spinel phase is present along with m + c-ZrO₂ at 800°C. Nucleation of γ -Al₂O₃ occurred in samples held at 1000°C. The γ -polymorph is a cubic polymorph with a spinel structure and the lattice parameter exactly matches that of the Al₂O₃-rich spinel. In previous work on rapidly solidified MgO-Al₂O₃ compositions, the γ -phase was found for Al₂O₃-rich compositions [18]. There is an anomaly in the RS spinel phase development during annealing compared with annealing single crystals or polycrystalline Al₂O₃-rich spinels. In single crystals ($x = 0.125-0.5$), it was reported that precipitation of Al₂O₃ occurs first by the nucleation of 10-nm crystallites, then by the formation of a platy monoclinic phase ($x = 0.06$) and finally the precipitation of α -Al₂O₃ [27-29]. No γ -Al₂O₃ was

Table 4

Summary of the results for the annealed RS Al₂O₃-MgO-ZrO₂ ternary eutectics

Composition	Annealing conditions (1 h)	Phases present
17.4MgO-42.1Al ₂ O ₃ -40.5ZrO ₂ (Al ₂ O ₃ -rich)	800°C	Spinel + m + c-ZrO ₂
	1000-1200°C	Spinel + γ -Al ₂ O ₃ , m + c-ZrO ₂
	1400-1600°C	Spinel, γ + α -Al ₂ O ₃ , m + t + c-ZrO ₂
42.1MgO-16.6Al ₂ O ₃ -41.3ZrO ₂ (MgO-rich)	800-1000°C	Spinel + MgO + c-ZrO ₂
	1600°C	Spinel + MgO, m + t + c-ZrO ₂

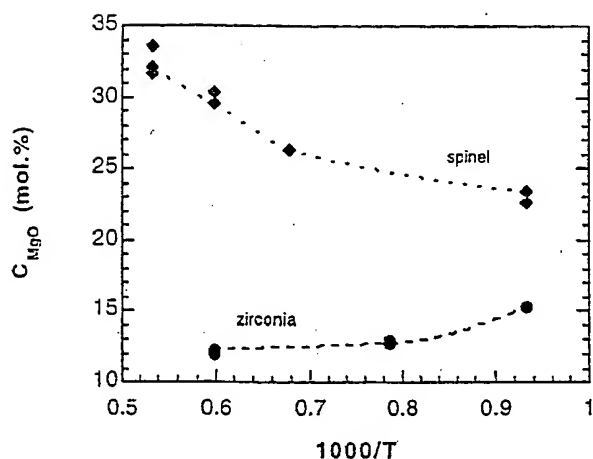


Fig. 5. Concentration of MgO in the spinel phase ($C_{\text{MgO}} = x$) and in c-ZrO₂ ($C_{\text{MgO}} = y$) as a function of annealing temperature.

found. In the work on the polycrystalline spinels ($x = 0.333$), it was found that $\alpha\text{-Al}_2\text{O}_3$ directly precipitates from the spinel and again no $\gamma\text{-Al}_2\text{O}_3$ was reported at $T \geq 1400^\circ\text{C}$ [30]. In the present study, nucleation of $\gamma\text{-Al}_2\text{O}_3$ initially occurred and $\alpha\text{-Al}_2\text{O}_3$ was found after annealing at 1400°C . In the polycrystalline work, the x -value was closer to stoichiometry whereas in the present work, x ranged from 0.221 to 0.340. It is also possible that the presence of c-ZrO₂ may have suppressed the nucleation of $\alpha\text{-Al}_2\text{O}_3$, since it was reported in the polycrystalline work that $\alpha\text{-Al}_2\text{O}_3$ nucleates on the surface of spinel. t-ZrO₂ was detected only under anneals at $T > 1400^\circ\text{C}$. This is consistent with the phase diagram which reports the eutectoid decomposition (c-ZrO₂ \rightarrow t-ZrO₂ + MgO) temperature at 1400°C .

Fig. 5 plots the concentration of MgO in the spinel phase and in c-ZrO₂ as a function of reciprocal temperature as determined from Eqs. (1) and (2). As shown, the MgO concentration increased in the spinel phase (from $x = 0.221$ to $x = 0.340$) and decreased in the ZrO₂ phase (from $y = 0.155$ to $y = 0.116$) as the temperature was raised. The MgO content increased in the spinel due to two factors: the nucleation of $\gamma\text{-Al}_2\text{O}_3$ and to a lesser extent to the MgO diffusion from c-ZrO₂ into the spinel phase. Diffusion of MgO from c-ZrO₂ resulted in the formation of t-ZrO₂, in accordance with the phase diagram. Fig. 2(b) pictorially shows the change in composition of the spinel after annealing the as-quenched material at 1600°C . The phase development during annealing follows what is predicted from the phase diagram, namely that an alumina phase will nucleate and co-exist with a spinel phase.

The fraction of m-ZrO₂ (f_m) is found from the XRD results by the ratio of the (111) and ($\bar{1}\bar{1}\bar{1}$) peak intensities for the three polymorphs:

$$f_m = \frac{I_m(111) + I_m(\bar{1}\bar{1}\bar{1})}{I_m(111) + I_m(\bar{1}\bar{1}\bar{1}) + I_t(111) + I_t(\bar{1}\bar{1}\bar{1})} \quad (4)$$

where I_m , I_t and I_c are the intensities of the 100% (111) or peaks. The fraction of m-ZrO₂ as a function of annealing temperature is plotted in Fig. 6. As shown, a small fraction of m-ZrO₂ is initially present, as discussed earlier. The amount does not change appreciably until the temperature is equal to or greater than 1200°C , where f_m increases and reaches about 0.8 at 1600°C . The t-ZrO₂ can subsequently transform to m-ZrO₂ from cooling if the grain size is large enough or from the stress induced t \rightarrow m transformation is produced from crushing the sample for powder X-ray work. Fig. 2(a) shows pictorially the compositional change after annealing at 1600°C . The as-quenched material composition falls in the c-ZrO₂ + MgO phase field and after annealing falls in the c-ZrO₂ field. However, upon cooling it is predicted that t + m-ZrO₂ will form.

For the heat-treated MgO-rich eutectic, spinel, MgO and c-ZrO₂ phases co-exist over a large temperature range for various annealing times. Only in samples held at 1600°C for is the presence of m + t-ZrO₂ detected along with c-ZrO₂. Fig. 7 shows the data from the annealing experiments on the MgO-rich eutectic. As shown, the MgO content in the spinel remains constant within experimental error over the annealing temperature range while the c-ZrO₂ shows a marked decrease in MgO concentration with increasing annealing temperature. No $\gamma\text{-Al}_2\text{O}_3$ or $\alpha\text{-Al}_2\text{O}_3$ was found under any annealing condition. This is in agreement with the results of Saalfeld and Jagodzinski [27,28] in which precipitation of an Al₂O₃ phase did not occur for slightly Al₂O₃-rich spinels. The MgO diffuses out of the c-ZrO₂ phase and into the MgO phase in accordance with the phase diagram. It has been shown that the eutectoid reaction c-ZrO₂ \rightarrow m-ZrO₂ + MgO occurs for $T \leq 1240^\circ\text{C}$ in a compositional range $x = 0.081 \rightarrow 0.186$ [31]. Although in the present work, m-ZrO₂ was not

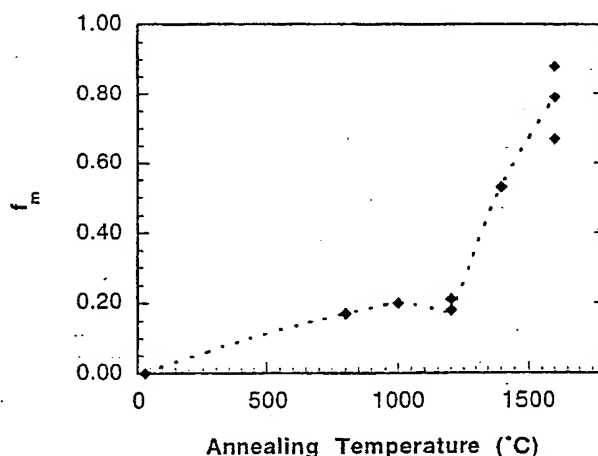


Fig. 6. Fraction of m-ZrO₂ as a function of annealing temperature in the Al₂O₃-rich eutectic.

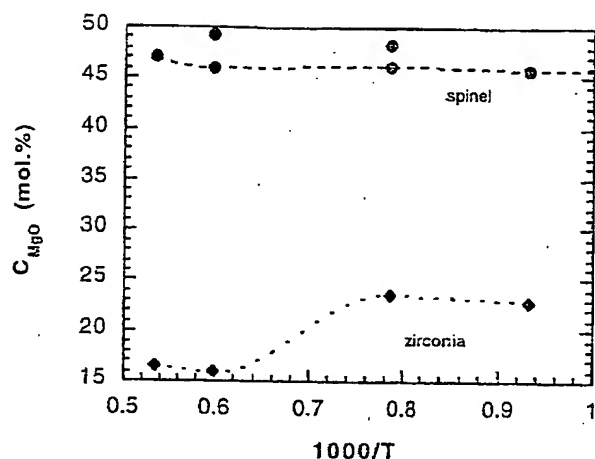


Fig. 7. Concentration of MgO in the spinel phase ($C_{\text{MgO}} = x$) and in c-ZrO₂ ($C_{\text{MgO}} = y$) as a function of heat-treatment temperature for the MgO-rich eutectic.

found at the low-temperature anneals, it may be due to the short annealing time coupled with the presence of the cubic spinel phase. Fig. 2(a) pictorially shows the compositional change of the zirconia phase after annealing at 1600°C. The starting composition falls in the c-ZrO₂ + MgO phase field and remains there after annealing. The t + m-ZrO₂ nucleate upon cooling from the high temperature.

For the spinel phase, the calculated as-quenched composition ($x = 0.462$) is nearly the stoichiometric one; however, as indicated earlier, there is uncertainty as to the exact lattice parameter of stoichiometric spinel in this work. It is assumed that during annealing at high enough temperatures, the spinel composition would go to equilibrium and maintain a stoichiometric composition. Starting with 46.2 mol% MgO, a change of 3.8 mol% would yield a difference in lattice parameter of 0.0019 nm, which is a measurable amount by X-ray diffraction. Since this was not measured, it is possible that the as-quenched composition was closer to the stoichiometric one.

4. Conclusions

Rapid solidification resulted in diverse compositional and structural phase assemblages in MgO-Al₂O₃-ZrO₂ eutectics. In the Al₂O₃-rich eutectic, rapid solidification resulted in the suppression of the primary Al₂O₃ phase and the formation of an Al₂O₃-rich spinel (22.1 mol% MgO) and c-ZrO₂ (15.5 mol% MgO). The characteristic lamellar microstructure of eutectics was observed. A metastable binary eutectic was found between these two phases and had the same composition as the ternary eutectic. Annealing these materials resulted in the formation of γ -Al₂O₃ which grew by depleting the Al₂O₃-rich spinel of Al₂O₃. After annealing at 1600°C for 1 h,

the MgO content in the spinel increased to 34 mol% and α -Al₂O₃ was detected. The composition of the spinel changes due to two factors: nucleation of γ -Al₂O₃ and to a lesser extent diffusion of MgO out of the c-ZrO₂. The MgO concentration in the zirconia decreased to 11.6 mol%.

For the MgO-rich ternary eutectic, rapid solidification yielded a three-phase assemblage of MgO, a nearly stoichiometric spinel (46.2 mol% MgO) and c-ZrO₂ (22.2 mol% MgO). Annealing these materials results in the growth of the MgO phase from diffusion of MgO out of c-ZrO₂. The spinel composition did not change significantly. Depletion of MgO from the c-ZrO₂ results in the eventual formation of t-ZrO₂, but only after annealing at 1600°C.

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